

Excitation Spectrum and Superexchange Pathways in the Spin Dimer $\text{VODPO}_4 \cdot 1/2\text{D}_2\text{O}$

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Magnetic excitations have been investigated in the spin dimer material $\text{VODPO}_4 \cdot 1/2\text{D}_2\text{O}$ using inelastic neutron scattering. A dispersionless magnetic mode was observed at an energy of 7.81(4) meV. The wavevector dependence of the scattering intensity from this mode is consistent with the excitation of isolated V^{4+} spin dimers with a V-V separation of 4.43(7) Å. This result is unexpected since the V-V pair previously thought to constitute the magnetic dimer has a separation of 3.09 Å. We identify an alternative V-V pair as the likely magnetic dimer, which involves superexchange pathways through a covalently bonded PO_4 group. This surprising result casts doubt on the interpretation of $(\text{VO})_2\text{P}_2\text{O}_7$ as a spin ladder.

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One of the goals of modern condensed matter physics is the comprehensive understanding of the ground state structure and excitations in quantum magnetic systems. Low dimensional systems, including spin chains, planes, and intermediate dimensional spin ladders are of particular importance because of the role they may play in the physics of high- T_C superconductors [1]. The exchange coupled spin dimer is the simplest interacting quantum magnetic system. Spin dimers can be thought of as the basic building blocks for more complicated spin systems, including RVB spin liquids and spin ladders. In this Letter we present the results of a neutron scattering study of excitations in a dimer system of particular interest: deuterated vanadyl phosphate demihydrate, $\text{VODPO}_4 \cdot 1/2\text{D}_2\text{O}$, (abbreviated VODPO). VODPO is closely related to the compound $(\text{VO})_2\text{P}_2\text{O}_7$ (VOPO) [2,3], which is widely thought to be an excellent realisation of the two-leg antiferromagnetic Heisenberg spin ladder. The present results show that there has been a fundamental misunderstanding of the magnetism in these materials, and that a careful re-examination of conclusions drawn about VOPO is called for. In particular the dominant exchange couplings have been misidentified.

The spin ladder nature of VOPO was proposed because the crystal structure contains $S = 1/2$ V^{4+} ion "rung" pairs which are stacked into ladders [2]. Magnetic interactions were thought to occur through V-O-V superexchange paths along both rung and chain directions. Neighbouring ladders are separated by PO_4 complexes which have been assumed to be magnetically inert. $(\text{VO})_2\text{P}_2\text{O}_7$ can be synthesized by dehydration of the precursor material $\text{VOHPO}_4 \cdot 1/2\text{H}_2\text{O}$ (VOHPO) [4,5]. VOHPO contains V-V pairs identical to the proposed

rungs of the VOPO ladder, but magnetically decoupled along the chain direction (see Fig. 1). It is therefore possible to study part of the ladder in isolation in VOHPO or the deuterated counterpart VODPO. For neutron scattering experiments the deuterated material has the advantage of lowering the incoherent background without significantly altering the magnetic interactions.

An idealized isotropic spin-dimer material consists of isolated pairs of magnetic ions that interact through a Heisenberg Hamiltonian,

$$H = J \vec{S}_1 \cdot \vec{S}_2 . \quad (1)$$

Johnson *et al.* [5] measured the magnetic susceptibility of VOHPO and found that it is accurately described by the Bleaney-Bowers formula for the susceptibility of isolated dimers of $S = 1/2$ spins, with $J = 7.6$ meV and $g = 1.99$ (close to the free electron value, as expected for an orbitally quenched V^{4+} ion).

By measuring the E and Q dependence of magnetic excitations using inelastic neutron scattering we can test this simple Hamiltonian and deduce the distance between V-V ion pairs in a dimer. Since a dimer has an $S_{\text{total}} = 0$ ground state and only one excited level (an $S_{\text{total}} = 1$ triplet at $E_1 - E_0 = J$), inelastic neutron scattering should reveal a single, dispersionless excitation. The susceptibility fit predicts that this excitation should appear at $E_{\text{gap}} = 7.6$ meV.

On carrying out a powder average over the neutron scattering structure factor $S(\vec{Q}, E)$ of a dimer, the powder scattering intensity $I(Q, E)$ is found to be [6]

$$I(Q, E) \propto |F(Q)|^2 \left(1 - \frac{\sin QR}{QR} \right) \delta(E - E_{\text{gap}}) . \quad (2)$$

Although we expect only a single excited level, the Q dependence of the magnetic excitation is especially interesting in that it allows a determination of the separation R of the magnetic ions forming the dimer pair.

The VODPO used in this study was synthesised from V_2O_5 , D_3PO_4 , and D_2O , which were refluxed under nitrogen for 2 days to obtain $VOPO_4 \cdot 2D_2O$. This product was heated in a Teflon-lined reaction vessel, with isopropanol- d_8 under nitrogen and autogenous pressure at 125° for 7 days, and then was filtered and dried in a nitrogen glove bag to obtain VODPO. Infrared spectroscopy indicated an H/D ratio of 0.04.

Neutron powder diffraction was used to refine the crystal structure, which gave parameters similar to previous results for VOHPO [4]. Rietveld refinement yielded an orthorhombic structure at $T = 10$ K, with lattice parameters of $a = 7.4102(6)$ Å, $b = 9.5861(8)$ Å, and $c = 5.6873(7)$ Å. It also confirmed the atomic fraction of deuterium as being at least 96%. The crystal structure of VODPO at 10 K is illustrated in Figure 1a. The structure contains V^{4+} ions, each of which has a single $3d$ electron and effective spin $S = 1/2$. Neighboring V^{4+} ions belong to edge-sharing VO_6 octahedra. Next-nearest-neighbor V^{4+} ions are separated by PO_4 tetrahedra.

Possible exchange paths between neighboring V^{4+} ions are shown in Figure 1b. The nearest-neighbor pathway (P1) has a V-V separation of $d_{VV} = 3.09$ Å and the next-nearest-neighbor pathway (P2) has a V-V separation of $d_{VV} = 4.32$ Å. Consideration of orbital overlaps led Beltrán-Porter *et al.* [7] to conclude that superexchange in VODPO is probably dominated by the P1 pathway.

The magnetic excitation spectrum of VODPO was measured using the HB1 triple-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory. Approximately 10 grams of VODPO powder was sealed in an aluminum cylinder and mounted in a displacer cryostat, allowing the temperature to be varied over the range 10 K – 300 K, with an accuracy of ± 0.1 K. The Q resolution of the spectrometer was relaxed because the excitations were expected to be dispersionless. A vertically focussed PG(002) monochromator and horizontally focussed PG(002) analyser were used, and an instrumental collimation of $48'-40'$ -open-open was chosen. Measurements were made using a fixed final energy $E_F = 13.5$ meV, giving an energy resolution of 1.16 meV full-width half maximum (FWHM).

Scans in E at fixed Q were carried out in order to measure the magnetic excitations. Figure 2 shows the scattering at temperatures of 10 K, 50 K and 200 K, at a constant wavevector transfer of $Q = 1.0$ Å $^{-1}$. In each scan there is a well-defined peak near 7.8 meV, close to the value of 7.6 meV anticipated from the susceptibility data [5]. To extract accurate positions and widths for the peaks, a least-squares routine was used to fit a Gaussian profile with a linearly-sloping background. This

gave a peak center of $J = 7.86(6)$ meV and FWHM of 2.05(10) meV for the scan at 10 K. Peak centers, intensities and widths were extracted at the other temperatures using the same procedure. The integrated intensity falls with increasing temperature roughly as expected for a magnetic dimer mode.

To investigate the dispersion of this mode we carried out a series of scans at 10 K with increasing wavevector, covering the range $Q = 1.0$ -4.5 Å $^{-1}$, at intervals of $\Delta Q = 0.1$ Å $^{-1}$. Each scan was fitted to a Gaussian with linear background. The mode was found to be essentially non-dispersive, although the fitted width increases slightly with Q .

To find the dimer spacing d_{VV} , a constant energy scan was made at 7.75 meV. Figure 3 shows this scan at a temperature of 10 K. There are two clear maxima in the data, near 1.0 Å $^{-1}$ and 2.3 Å $^{-1}$; this oscillatory behavior is expected for scattering from a dimer, *cf.* Eq. (2). The solid line in the figure is a least-squares fit to Eq. (2), in which the $\langle J_0 \rangle$ approximation for the V^{4+} form factor [8] has been used. A sloping background has been added to take account of the phonon contribution, which increases with Q . The fit yields a V-V separation in the dimer of $d_{VV} = 4.43(7)$ Å, which we consider our definitive value.

Figure 4 shows a two-dimensional color plot of the combined constant- Q scans at 10 K. The data have been interpolated to smooth the image, and the intensity is indicated by a colorbar. The spin excitation is observed as a band at 7.8 meV, with maximum intensity at the lower wavevectors. Two maxima of the structure factor as a function of Q appear as bright regions near 1.0 Å $^{-1}$ and 2.3 Å $^{-1}$. The non-magnetic phonon background is visible at large Q , especially at energies above 8 meV. A simultaneous least-squares fit was made to Eq. (2) plus a background term linear in E and Q . The delta function in energy was replaced by a Gaussian lineshape. The global fit gave an excellent description of the data with $J = 7.81(4)$ meV, $d_{VV} = 4.49(8)$ Å, consistent with the 4.43(7) Å found in the constant- E scan in Figure 3. A goodness-of-fit reduced $\chi^2 = 1.12$. The fitted model is shown as a contour plot (solid lines) overlying the data in Figure 4.

Our constant- E measurement gave a dimer spacing of $d_{VV} = 4.43(7)$ Å, consistent with the exchange path P2 shown in Figure 1b ($d_{VV} = 4.32$ Å), but not with the shorter P1 exchange path ($d_{VV} = 3.09$ Å) assumed to be dominant in earlier work [5,7]. This is surprising because it implies that the exchange is stronger through a V-O-P-O-V pathway than through a much shorter V-O-V pathway. The conventional understanding of superexchange is that the interaction decreases rapidly with the number of ions in the exchange path [9]. We argue however that when there is a covalent complex present, such as the PO_4 in VODPO, coherent orbitals can provide a strong exchange route. Understanding the electron wavefunctions within such covalent groups is therefore crucial in

predicting the important superexchange pathways. Presumably the V-O-V superexchange is also weakened by the large departure of the bond angle (experimentally 97.5°) from the optimum 180° for -O-.

Beltrán-Porter *et al.* [7] have considered exchange pathways in several vanadyl phosphates. Although they did not anticipate a dominant PO_4 pathway in VODPO, they do argue that PO_4 pathways may be significant in $(\text{VO})_2\text{P}_2\text{O}_7$, as well as V-O-V. If V-O-V (rung) and V-O-P-O-V are the important exchange pathways in $(\text{VO})_2\text{P}_2\text{O}_7$, its magnetic Hamiltonian may be better approximated by an alternating chain than a ladder, with the alternating chain directed along the rung of the ladder (*cf.* Johnston *et al.* [2]). Our results on VODPO confirm the importance of PO_4 pathways, and our recent study of magnetic excitations in $(\text{VO})_2\text{P}_2\text{O}_7$ single crystals [10] appears to support an alternating-chain model.

In summary, we have used inelastic neutron scattering on a powder sample to study magnetic excitations in $\text{VODPO}_4 \cdot 1/2\text{D}_2\text{O}$. Our results support a magnetic dimer model for this system, with an exchange constant of $J = 7.81(4)$ meV, close to the value found in a susceptibility fit. The V-V spacing within the dimer however is found to be $4.43(7)$ Å, which indicates that the dimer pair has been misidentified in previous work. The dimer pair we identify has a V-O-P-O-V superexchange pathway through a PO_4 group, which evidently leads to a stronger magnetic interaction than the shorter V-O-V pathway.

Strong superexchange through covalently bonded inorganic complexes is presumably important in many magnetic insulators. For example, an exchange of ≈ 30 meV through WO_6 complexes has recently been identified in CuWO_4 [11] and -O-Mo-O- pathways have been noted in FeMoO_4Cl [12]. The various topologies of covalent groups should allow the synthesis of a wide range of low-dimensional magnetic materials [13].

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Figure Captions

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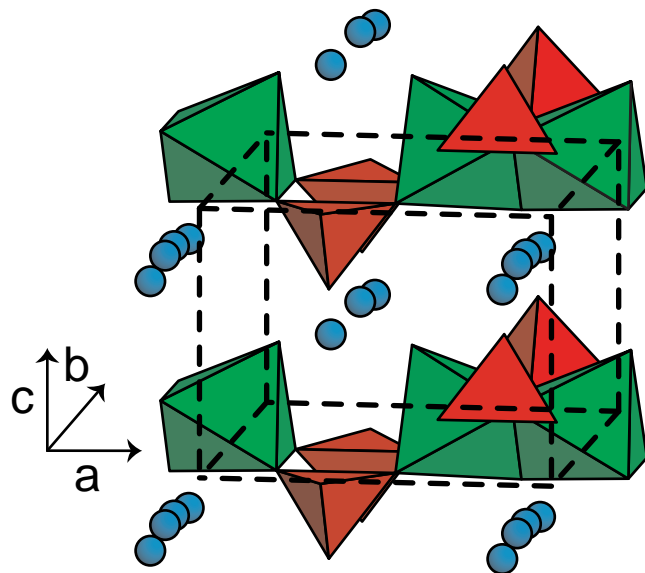
Fig.1. (color) (a) The structure of VODPO at 10K is shown. Edge-sharing VO_6 octahedra (green) are connected by PO_4 tetrahedra (red). These layers are separated by D atoms (grey). An orthorhombic unit cell is indicated by the dashed line, and the crystal axes are indicated at lower left. (b) This shows a schematic projection of the crystal structure in the $a-b$ plane illustrating possible superexchange pathways between V^{4+} ions. V ions are shown in green, P in red, and O in blue. P1 is a V-O-V pathway ($d_{\text{VV}}=3.09 \text{ \AA}$), and P2 is V-O-P-O-V ($d_{\text{VV}}=4.32 \text{ \AA}$).

Fig.2. Scans in energy at a constant wavevector transfer of $Q = 1.0 \text{ \AA}^{-1}$ are displayed. The data are scaled to a fixed number of incident neutrons, as determined by a monitor counter. Monitor 100 corresponds to roughly 1 minute of counting time per point. The error bars represent one standard deviation. The profiles at different temperatures have been offset by a constant number of counts for clarity of presentation. The solid lines are fits to a Gaussian plus a sloping background as discussed in the text.

Fig.3. A scan in wavevector transfer Q at a constant energy transfer of 7.75 meV (essentially the dimer excitation energy) is shown, with some representative error bars. The solid line is a fit to the dimer model, as described in the text.

Fig.4. (color) This shows a two-dimensional color plot of the combined constant- Q scans. The contour lines are the results of the global fit described in the text. Counts per monitor 100 are given by the colorbar.

(a)



(b)

